

PATENT ABSTRACTS OF JAPAN

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(54) NONAQUEOUS ELECTROLYTE BATTERY

(57)Abstract:

PURPOSE: To provide an excellent nonaqueous electrolyte battery which has no danger such as burst and fire during trouble in short by using solution that lithium salt is dissolved in phosphagen derivative or solution that lithium salt is dissolved in solvent that nonprotic organic solvent is further added to phosphagen derivative, as electrolyte.

CONSTITUTION: In a nonaqueous electrolyte battery which is formed with a positive plate, a negative plate possible to occlude and emit lithium and nonaqueous electrolyte containing lithium ions, solution that lithium salt is dissolved in phosphagen derivative with the viscosity of 300cP or less at 25°C or solution that lithium salt is dissolved in solvent that nonprotic organic solvent is further added to phosphagen derivative with the viscosity of 500cP or less at 25°C is used as the electrolyte.

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CLAIMS

[Claim(s)]

[Claim 1] The nonaqueous electrolyte cell characterized by the viscosity of 25 degrees C using the solution which dissolved lithium salt in the phosphazene derivative of 300 or less cPs as the above-mentioned electrolyte in the nonaqueous electrolyte cell which comes to provide a positive electrode, the negative electrode which can emit [occlusion and] a lithium, and the nonaqueous electrolyte containing a lithium ion.

[Claim 2] The nonaqueous electrolyte cell by which viscosity of 25 degrees C is characterized by using the solution which dissolved lithium salt in the solvent which added the aprotic organic solvent to the phosphazene derivative of 500 or less cPs further as the above-mentioned electrolyte in a cell according to claim 1.

[Claim 3] In a cell according to claim 1 or 2 the above-mentioned phosphazene derivative n (NPR2) (-- however, it has the chain combination of an annular mold phosphazene derivative, or the Lynn and nitrogen in which R is shown by the organic radical of monovalence and n is shown by 3 - 15) in a frame -- R3 (P=N) m-PR4 It is the nonaqueous electrolyte cell characterized by being the shape type phosphazene derivative of a chain shown [(however, 1-20R are chosen for m from the organic radical of monovalence, O or C), and].

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the nonaqueous electrolyte cell which also attained simultaneously the cell engine performance which was related with the nonaqueous electrolyte cell, and removed the burst especially at the time of a short circuit, and the danger of ignition, and was [capacity / high tension, / high discharge] excellent.

[0002]

[Description of the Prior Art] Since a nonaqueous electrolyte cell has the description of high tension and a high energy consistency and shows the outstanding self-discharge nature, it attracts attention dramatically especially in recent years as memory backup of AV and information machines and equipment, such as a personal computer and VTR, or those cells for actuation power sources. Moreover, although a nickel-cadmium battery is in use as a rechargeable battery used for these applications, as an alternative of this nickel-cadmium battery, development is tried also for various rechargeable battery-ization of a nonaqueous electrolyte cell, and that part is commercialized.

[0003] Although alkali metal especially the lithium metal, and the lithium alloy are used abundantly as an ingredient which forms the negative electrode of the above-mentioned nonaqueous electrolyte cell, in order that these may react violently with the drainage system electrolytic solution, as an electrolyte, the nonaqueous electrolyte cell which used organic solvents, such as an aprotic organic solvent, as the base, for example is used.

[0004]

[Problem(s) to be Solved by the Invention] Although a nonaqueous electrolyte cell is highly efficient as mentioned above, there is a problem in safety. Namely, to moisture, it is very high activity, for example, obturation of a cell is imperfect, in response to the time of moisture invading, hydrogen may occur or, as for the alkali metal used for the negative electrode of a nonaqueous electrolyte cell especially a lithium metal, a lithium alloy, etc., the above-mentioned negative-electrode ingredient and water may ignite.

[0005] Moreover, we are anxious about causing very dangerous situations -- since it is the low melting point (about 170 degrees C), if a high current flows rapidly at the time of a short circuit etc., a cell will generate heat unusually and, for this reason, a cell will fuse a lithium metal. Furthermore, the electrolytic solution which uses the above-mentioned organic solvent as the base along with generation of heat of a cell evaporates or decomposes, for this reason, gas occurs or the danger that the burst of a cell and ignition will be caused by this gas also becomes high.

[0006] for example, the solution which dissolved the positive electrode for the inorganic compound and dissolved lithium salt for the lithium metal in organic solvents, such as a negative electrode and an aprotic organic solvent, -- the electrolytic solution -- carrying out -- AA -- when the cartridge cell of a mold is produced and the external short circuit of the two poles of this cell is carried out, generation of heat of 150 degrees C or more may be seen, consequently a cell may explode, and it may result even in ignition eventually

[0007] Then, when temperature goes up at the time of the short circuit of a cell, and overcharge and the pressure inside a cell rises as an approach of securing the safety of a nonaqueous electrolyte cell, in the case of for example, a cartridge cell, preparing in a cell a device which inhibits that the excessive current beyond a predetermined current flows on a cell is proposed by making an electrode terminal fracture at the same time a relief valve operates.

[0008] However, when such all devices cannot trust it and it does not operate well, we are anxious about generation of heat by the excessive current becoming large, and being in a dangerous condition, and it is hard to be referred to as that still sufficient security is made.

[0009] In such a viewpoint, the appearance of the nonaqueous electrolyte cell instead of the safety practice by preparing supplementary components, such as a relief valve, as mentioned above which demonstrates safety equivalent to the lead cell and nickel-cadmium battery which are a drainage system electrolyte cell by devising and improving a cell

ingredient fundamentally is expected.

[0010] It aims at offering the nonaqueous electrolyte cell which this invention was made in view of the above-mentioned situation, controls evaporation of the electrolytic solution in low temperature, and decomposition comparatively, and reduces the danger of ignition and ignition simultaneously, and has the outstanding cell engine performance.

[0011]

[Means for Solving the Problem and its Function] In the nonaqueous electrolyte cell which comes to provide a positive electrode, the negative electrode which can emit [occlusion and] a lithium, and the nonaqueous electrolyte containing a lithium ion as a result of inquiring wholeheartedly, in order that this invention person may attain the above-mentioned object As the above-mentioned electrolyte, the viscosity of 25 degrees C uses the solution which dissolved lithium salt in the phosphazene derivative of 300 or less cPs, Moreover, when the viscosity of 25 degrees C uses the solution which dissolved lithium salt in the solvent which added the aprotic organic solvent to the phosphazene derivative of 500 or less cPs further as the above-mentioned electrolyte The nonaqueous electrolyte cell which has the cell engine performance which could control evaporation of the electrolytic solution in low temperature and decomposition comparatively, and could reduce the danger of ignition and ignition simultaneously, and was [nature / high tension, high discharge capacity, / high current discharge] excellent is obtained, Moreover, when a phosphazene derivative and an aprotic solvent were mixed, it found out that it stops being able to burn easily since a protonic organic solvent coexists with a phosphazene derivative, and it could control a burst and ignition.

[0012] Namely, it is hard to cause evaporation and decomposition at the temperature of 200 degrees C or less from a viewpoint of the fundamental security of a nonaqueous electrolyte cell. It will not be burned down by a spreading fire even if there is ignition inside a cell by melting of the lithium which is a negative-electrode ingredient etc. And when it searches for many things as a solvent which has conductivity equivalent to the existing electrolyte paying attention to an inorganic polymer ingredient, the knowledge of it being dramatically promising using the derivative of phosphazene with which a basic frame consists of nitrogen and Lynn as a constituent of the electrolytic solution is carried out, and it comes to make this invention.

[0013] In addition, although the application to the cell ingredient of a phosphazene compound has conventionally the example of all the solid state batteries that use polyphosphazene (methoxyethoxy ethoxy polyphosphazene, oligoethyleneoxy polyphosphazene, etc.) as a solid electrolyte and fire-resistant effectiveness can be dramatically expected in this case, the achievement of a cycle property which ion conductivity was limited only to 1 / 1000 - 1/10000, or the activity in the low discharge current which becomes and was low and was restricted as compared with the usual liquefied electrolyte, and was excellent is difficult. The electrolytic solution used it, having carried out the constituent of the phosphazene derivative liquefied as mentioned above, and the new knowledge by this invention person attained conductivity equivalent to the usual liquefied electrolyte, and the outstanding cycle property.

[0014] Therefore, in the nonaqueous electrolyte cell which comes to provide a positive electrode, the negative electrode which can emit [occlusion and] a lithium, and the nonaqueous electrolyte containing a lithium ion, the solution which dissolved lithium salt in the solvent with which the solution with which the viscosity of 25 degrees C dissolved lithium salt in the phosphazene derivative below 300cP(s) (centipoise), or the viscosity of 25 degrees C added the aprotic organic solvent to the phosphazene derivative of 500 or less cPs further is used for this invention as the above-mentioned electrolyte.

[0015] Hereafter, if this invention is explained in more detail, the solution which dissolved lithium salt in the solvent with which the solution with which the viscosity of 25 degrees C dissolved lithium salt in the phosphazene derivative of 300 or less cPs as mentioned above, or the viscosity of 25 degrees C added the aprotic organic solvent to the phosphazene derivative of 500 or less cPs further will be used for the electrolyte of the nonaqueous electrolyte cell of this invention.

[0016] Here as a phosphazene derivative which is an electrolytic-solution solvent For example, (NPCl₂)_n which permuted the chlorine of n by the various substituents R (NPR₂) The annular mold phosphazene derivative expressed with (however, n is 3-15), It has the chain combination of a phosphoric acid and nitrogen in a basic frame, and the side chain radical R was added, for example, (R₃ (P=N) m-PR₄) (however, 1-20R are chosen for m from the organic radical of monovalence, O, or C) two persons of the shape type phosphazene derivative of a chain shown are mentioned to Lynn.

[0017] In this case, a substituent or a side chain radical R is an organic radical of monovalence, and becomes compoundable [the solvent which has the proper viscosity which can be equal to an activity as the electrolytic solution, and the solubility suitable for mixing] by choosing R moderately. Although the dissolution mechanism of the lithium salt to a phosphazene solvent is still unknown, to have the shape of a solution with comparatively low viscosity as a

phosphazene derivative, and to be the structure where lithium salt may be dissolved good is desired. For this reason, as for a substituent or a side chain radical R, it is advantageous to include ether linkage, and it is also possible to be able to mention an alkoxy group or alkoxy permutation alkoxy groups, such as an ethoxy radical, a propoxy group, a butoxy radical, and a methoxyethoxy ethoxy radical, etc. as such R, and to replace the hydrogen in the above-mentioned substituent or a side chain radical by halogens, such as a fluorine and boron.

[0018] For example, in the phosphazene derivative (NPR₂) 3 of an annular mold, the viscosity in 25 degrees C is 60cP (s), the phosphazene derivative whose R is a propoxy group can serve as a solvent suitable as the electrolytic solution, and to 1kg of phosphazene derivatives, the solubility of lithium salt is also possible to about 0.5 mols, and can demonstrate the very good lithium ion conductivity which is equal compared with the common organic solvent system electrolytic solution.

[0019] On the other hand, in what added the propoxy group to the both-ends section of P=N-P structure in the shape type phosphazene derivative of a chain which has the chain combination of Lynn and nitrogen in a basic frame, the viscosity in 25 degrees C can be reduced up to about 30 cP(s), hypoviscosity-ization can be attained more as compared with the above-mentioned annular mold, and the lithium salt solubility to about one mol is simultaneously acquired to 1kg of phosphazene derivatives. It is desirable to use a shape of chain type phosphazene derivative as an electrolyte from the above thing.

[0020] When an aprotic organic solvent is not used for the above-mentioned phosphazene derivative, especially the viscosity in 25 degrees C uses the thing of 100 or less cPs below 300 centipoises (cP). Ion conductivity falls remarkably according to buildup of the viscous drag of a solution, and it becomes deficient in performance in an activity at the low temperature below the freezing point at the same time it will be hard coming to dissolve lithium salt and the wettability to a positive-electrode ingredient and a separator will also fall, if the viscosity of a phosphazene derivative exceeds 300cP(s).

[0021] In this invention, what mixed the aprotic organic solvent further to the above-mentioned phosphazene derivative can also be used as an electrolytic-solution solvent. In this case, although especially an aprotic organic solvent is not limited, ether compounds, ester compounds, etc., such as 1, 2-dimethoxyethane, a tetrahydrofuran, and propylene carbonate, are used suitably, for example.

[0022] Moreover, although the phosphazene derivative used here can use the same thing as the above, 500 or less cPs especially of viscosity in 25 degrees C are set to 300 or less cPs. If this viscosity exceeds 500cP(s), even after mixing with an aprotic organic solvent, it becomes hyperviscosity, and it becomes difficult to attain the ion conductivity optimal as a nonaqueous electrolyte cell for this reason.

[0023] As for the rate of the phosphazene derivative mixed to an aprotic solvent, it is desirable to make it the volume fraction to the whole mixed solvent, and to consider as 50% or more and 90% or less. There is a case where the effectiveness that the rate of a phosphazene derivative controls the burst of a cell and ignition at less than 50% becomes less enough. Since it becomes near on the other hand when a phosphazene derivative is used independently if this rate exceeds 90%, the viscosity of a solution may increase, the lithium ion conductivity which is suitable for high current discharge when the phosphazene derivative with which the viscosity in 25 degrees C exceeds 300cP(s) for this reason is used may become difficult to get, and it may become deficient in performance in an activity at the low temperature below the freezing point.

[0024] one sort chosen from LiClO₄, LiBF₄, LiPF₆, LiCF₃SO₃, and LiAsF₆ although not limited especially as lithium salt which dissolves in the mixed solvent of the lithium salt used as a source of a lithium ion, i.e., a phosphazene derivative independent solvent, and a phosphazene derivative and an aprotic solvent -- or two or more sorts are used suitably. As for the addition of this lithium salt, it is desirable to consider as 0.2-1 mol to the 1kg of the above-mentioned solvents.

[0025] As a positive-electrode ingredient of the above-mentioned cell, conductive polymers, such as metallic sulfide of the metallic oxide of V₂O₅, V₆O₁₃, MnO₂ and MoO₃, and LiCoO₂ grade, TiS₂, and MoS₂ grade and the poly aniline, etc. can be used.

[0026] Moreover, although a negative-electrode ingredient contains a lithium, carbon materials, such as a graphite which specifically doped the lithium metal, the lithium, and an alloy with aluminum, an indium, lead, zinc, etc. and a lithium, etc. can be used.

[0027] Since the short circuit of the current by contact of two poles is prevented between the above-mentioned forward negative electrodes, a separator can be made to intervene in the nonaqueous electrolyte cell of this invention. Although the nonwoven fabric made of synthetic resin, such as the ingredient which can prevent contact of two poles certainly, and, and contains or is made as a separator, for example, polytetrafluoroethylene, polypropylene, and polyethylene, a thin layer film, etc. can be mentioned, polypropylene with a thickness of about 20-50 micrometers or the microporous

film made from polyethylene is used especially preferably. [letting the electrolytic solution pass]

[0028] In addition, as a configuration member of others of this invention cell, what is usually used can be used convenient. Moreover, especially the gestalt of a cell is not restricted but can take various gestalten, such as a telescopic cell of a coin type, a carbon button type, a paper type, a square shape, or spiral structure.

[0029]

[Example] Although an example and the example of a comparison are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example.

[0030] Let the banazin san ghost shown with examples 1-3 and the [examples 1 and 2 of comparison] chemical formula LiV_3O_8 be positive active material. After having used, having added acetylene black as an electric conduction assistant, adding the Teflon binder the 10 sections as the ten sections and a binder to the $3\text{OLiV}_8\text{100}$ section and kneading with an organic solvent (ethyl acetate, and 50 / 50 volume % mixed solvent of ethanol), the positive-electrode sheet of the shape of a thin layer with 100 micrometers [in thickness] and a width of face of 40mm was produced with roll rolling.

[0031] Next, aluminium foil with a thickness of 25 micrometers was used as the charge collector, this charge collector that applied electroconductive glue to the front face with the above-mentioned positive-electrode sheet of two sheets was put, the lithium metallic foil with a thickness of 150 micrometers was piled up and wound up through the separator which becomes this from the microporous film with a thickness of 25 micrometers made from polypropylene, and the spiral structure electrode was produced. At this time, positive-electrode die length was about 260mm.

[0032] this spiral structure electrode -- AA -- the electrolyte which dissolved LiPF_6 in five kinds of each electrolytic-solution solvent which holds in a mold container and is shown in a table 1 by the concentration of 0.5 mols/kg -- pouring in -- obturating -- five kinds of AA -- it assembled the mold lithium cell ten each at a time.

[0033] Here, phosphazene-No.1 which is the phosphazene derivative used as an electrolytic-solution solvent is obtained by permuting the chlorine with cyclic structure (NPCl_2) of n (however, n 3-5) by three $-\text{OCH}_2\text{CH}_2\text{CH}(\text{s})$. Phosphazene No.2 were set to have the chain structure ($\text{R13 P}=\text{N}-\text{P}(\text{O})\text{R22}$), and they used the thing whose R1 is three $-\text{OCH}_2\text{CF}$ and whose R2 is $-\text{OC}_2\text{H}_5$ set. moreover, phosphazene No. -- 3 and 4 can twist the chlorine with the same cyclic structure as No.1 (NPCl_2) of n (however, n 3-5) in permuting by $-\text{CH}_2\text{CF}_2\text{CF}_3$ and $-\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$ set.

[0034] About five kinds of cells produced as mentioned above, the early cell property (an electrical potential difference, internal resistance) was evaluated, and the charge-and-discharge cycle engine performance, high-rate-discharge nature (current dependency of discharge capacity), and safety were evaluated by the following appraisal method. A result is shown in a table 1.

[0035] (Appraisal method) Charge and discharge were repeated up to 50 cycles on the conditions of charge-and-discharge cycle property upper limit electrical-potential-difference 3.0V, minimum electrical-potential-difference 2.0V, 100mA of discharge currents, and 50mA of charging currents, the capacity retention to the early stages of the event was investigated, and the three-cell average was shown.

[0036] After performing the charge and discharge of 5 cycle high-rate-discharge nature and charging to 3.0V, it discharged by 50mA first, and it charged again and discharged by 500mA succeedingly. It performed this actuation at a time about two cells, the discharge capacity in each current value was calculated, and it asked for capacity retention by (500mA from discharge capacity)/at the time of discharge (it is the discharge capacity at the time of discharge at 500mA).

[0037] After performing the charge and discharge of 5 cycle safety and charging to 3.0V, the external short circuit of the positive/negative two poles was connected and carried out with lead wire, and the existence of change of a cell appearance and burst ignition was checked using five cells.

[0038]

[A table 1]

		電 解 液 溶 媒		電池初期特性		サイクル性能			高 率 放 電 性			安 全 性
		溶 媒 種	粘 度 (cP)	電 圧 (V)	内 部 抵 抗 (mΩ)	初 期 (mAh)	50サイ クル (mAh)	保持率 (%)	50mA (mAh)	500mA (mAh)	保持率 (%)	
実 施 例	1	ホスファゼン No.1	60	3.32	210	745	708	95	745	660	89	全く異常 なし
	2	ホスファゼン No.2	35	3.33	190	755	725	96	755	685	91	全く異常 なし
	3	ホスファゼン No.3	100	3.28	220	750	705	94	750	660	88	全く異常 なし
比 較 例	1	ホスファゼン No.4	400	3.26	400	690	585	85	690	470	68	全く異常 なし
	2	プロピレン カーボネート + エチレンカー ボネート*	20	3.33	180	760	730	96	760	690	91	3本： 液もれ発生 2本： 破裂発火

*両溶媒を50体積%ずつ混合

[0039] The conventional cell using the organic solvent as an electrolytic-solution solvent as shown in a table 1 (example 2 of a comparison), As for the cell (examples 1-3) using the phosphazene derivative of moderate viscosity as an electrolytic-solution solvent, it turns out to having caused a liquid spill, a burst, and ignition at the time of a short circuit that it is not inferior even if it compares with the conventional cell using an organic solvent about it is completely normal and dramatically safe and the cell engine performance also at the time of a short circuit.

[0040] In the example 2 using the phosphazene derivative which has the chain structure especially, internal resistance is low and it is admitted that the cell engine performance is also most excellent.

[0041] Moreover, although abnormalities, such as ignition, were not seen like examples 1-3 at the time of a short circuit by the cell (example 1 of a comparison) using the phosphazene derivative with which viscosity exceeds 300cP(s) as an electrolytic-solution solvent, since solvent viscosity is too high, the discharge capacity under a high current is in the inclination to decrease considerably and for the cycle engine performance to be also inferior.

[0042] The cell which has the same structure as examples 1-3 was assembled using the electrolyte which dissolved LiPF₆ in the same positive-electrode ingredient and same negative-electrode ingredient as examples 4-7 and the [example 3 of comparison] examples 1-3, and five kinds of each electrolytic-solution solvent shown in a table 2 by the concentration of 0.5 mols/kg every ten per one kind of above-mentioned electrolytic-solution solvent.

[0043] Here, as a phosphazene derivative, it is at examples 4-6, Using what was obtained by permuting the chlorine with cyclic structure (NPCl₂) of n (however, n 3-5) by three -OCH₂CH₂CH(s), in the example 7, it set with the chain structure (R₁₃ P=N-P (O) R₂₂), and the thing whose R₁ is three -CH₂CF and whose R₂ is -OC₂H₅ set was used.

[0044] As a nonprotic solvent mixed with a phosphazene derivative, 1 and 2-dimethoxyethane was chosen, the mixing ratio with a phosphazene derivative was changed, and electrolysis solvent liquid was prepared. Moreover, the electrolytic-solution solvent used in the example 3 of a comparison consists only of a nonprotic solvent, and used the mixture of 1 and 2-dimethoxyethane and propylene carbonate.

[0045] The same assessment as an example 1 was performed about five kinds of cells produced as mentioned above. A result is written together to a table 2.

[0046]

[A table 2]

		電 解 液 溶 媒		電池初期特性		サイクル性能			高 率 放 電 性			安 全 性
		溶 媒 種 (体積%/体積%)	粘 度 (cP)	電 圧 (V)	内 部 抵 抗 (mΩ)	初 期 (mAh)	50サイ クル (mAh)	保持率 (%)	50mA (mAh)	500mA (mAh)	保持率 (%)	
実 施 例	4	環状構造ホスファゼン誘導体/ 1,2-ジメトキシエタン (60/40)	18	3.28	150	765	730	95	765	705	92	全く異常なし
	5	環状構造ホスファゼン誘導体/ 1,2-ジメトキシエタン (75/25)	24	3.32	170	760	720	95	760	685	90	全く異常なし
	6	環状構造ホスファゼン誘導体/ 1,2-ジメトキシエタン (85/15)	32	3.24	185	760	705	93	760	675	89	全く異常なし
	7	鎖状構造ホスファゼン誘導体/ 1,2-ジメトキシエタン (85/15)	13	3.30	140	760	730	96	760	705	93	全く異常なし
比 較 例	3	プロピレンカーボネート/1,2-ジメトキシエタン (50/50)	10	3.30	140	770	740	96	770	725	94	2本： 液もれ発生 3本： 破裂発火

[0047] The cell using the electrolytic-solution solvent which consists only of an aprotic organic solvent as shown in a table 2 (example 3 of a comparison), As for the cell (examples 4-7) using the mixture of a phosphazene derivative and an aprotic organic solvent as an electrolytic-solution solvent, it turns out to having caused a liquid spill, a burst, and ignition at the time of a short circuit that it is not inferior even if it compares with the conventional cell using an organic solvent about it is completely normal and dramatically safe and the cell engine performance also at the time of a short circuit.

[0048] When an example 6 and an example 7 with the same mixing ratio with a nonprotic solvent are compared especially, it is admitted that the level which the electrolysis solvent of hypoviscosity was obtained rather than the example 6 using the phosphazene derivative in which the direction of the example 7 using a phosphazene derivative with the chain structure has cyclic structure, and was more excellent also as cell engine performance can be attained.

[0049]

[Effect of the Invention] Since the solution which dissolved lithium salt in the solvent which added the aprotic organic solvent to the solution or phosphazene derivative which dissolved lithium salt in the phosphazene derivative as an electrolyte further is being used for the nonaqueous electrolyte cell of this invention, it can attain the cell engine performance which does not have danger, such as a burst and ignition, at the time of abnormalities, such as a short circuit,, either, and was excellent in it.

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CORRECTION OR AMENDMENT

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[Procedure amendment]

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[Procedure amendment 1]

[Document to be Amended] Description

[Item(s) to be Amended] Claim

[Method of Amendment] Modification

[Proposed Amendment]

[Claim(s)]

[Claim 1] The nonaqueous electrolyte cell characterized by the viscosity of 25 degrees C using the solution which dissolved lithium salt in the phosphazene derivative of 300 or less cPs as the above-mentioned electrolyte in the nonaqueous electrolyte cell which comes to provide a positive electrode, the negative electrode which can emit [occlusion and] a lithium, and the nonaqueous electrolyte containing a lithium ion.

[Claim 2] The nonaqueous electrolyte cell by which viscosity of 25 degrees C is characterized by using the solution which dissolved lithium salt in the solvent which added the aprotic organic solvent to the phosphazene derivative of 500 or less cPs further as the above-mentioned electrolyte in a cell according to claim 1.

[Claim 3] The nonaqueous electrolyte cell characterized by being the annular mold phosphazene derivative in which the above-mentioned phosphazene derivative is shown by n (however, R the organic radical of monovalence and n 3-15) (NPR2) in a cell according to claim 1 or 2.

[Procedure amendment 2]

[Document to be Amended] Description

[Item(s) to be Amended] 0016

[Method of Amendment] Modification

[Proposed Amendment]

[0016] Here, the annular mold phosphazene derivative expressed with n (NPR2) (however, n is 3-15) which permuted the chlorine of n by the various substituents R, for example (NPCl2) as a phosphazene derivative which is an electrolytic-solution solvent is mentioned.

[Procedure amendment 3]

[Document to be Amended] Description

[Item(s) to be Amended] 0017

[Method of Amendment] Modification

[Proposed Amendment]

[0017] In this case, Substituent R is an organic radical of monovalence and becomes compoundable [the solvent which has the proper viscosity which can be equal to an activity as the electrolytic solution, and the solubility suitable for mixing] by choosing R moderately. Although the dissolution mechanism of the lithium salt to a phosphazene solvent is still unknown, to have the shape of a solution with comparatively low viscosity as a phosphazene derivative, and to be the structure where lithium salt may be dissolved good is desired. For this reason, as for Substituent R, it is advantageous to include ether linkage, and it is also possible to be able to mention an alkoxy group or alkoxy permutation alkoxy groups, such as an ethoxy radical, a propoxy group, a butoxy radical, and a methoxyethoxy ethoxy radical, etc. as such R, and to replace the hydrogen in the above-mentioned substituent by halogens, such as a fluorine and a bromine.

[Procedure amendment 4]

[Document to be Amended] Description

[Item(s) to be Amended] 0019

[Method of Amendment] Deletion

[Procedure amendment 5]

[Document to be Amended] Description

[Item(s) to be Amended] 0023

[Method of Amendment] Modification

[Proposed Amendment]

[0023] As for the rate of the phosphazene derivative mixed to an aprotic solvent, it is desirable to make it the volume fraction to the whole mixed solvent, and to consider as 90% or less 50% or more. There is a case where the effectiveness that the rate of a phosphazene derivative controls the burst of a cell and ignition at less than 50% becomes less enough. Since it becomes near on the other hand when a phosphazene derivative is used independently if this rate exceeds 90%, the viscosity of a solution may increase, the lithium ion conductivity which is suitable for high current discharge when the phosphazene derivative with which the viscosity in 25 degrees C exceeds 300cP(s) for this reason is used may become difficult to get, and it may become deficient in performance in an activity at the low temperature below the freezing point.

[Procedure amendment 6]

[Document to be Amended] Description

[Item(s) to be Amended] 0032

[Method of Amendment] Modification

[Proposed Amendment]

[0032] this spiral structure electrode -- AA -- the electrolyte which dissolved LiPF₆ in four kinds of each electrolytic-solution solvent which holds in a mold container and is shown in a table 1 by the concentration of 0.5 mols/kg -- pouring in -- obturating -- four kinds of AA -- it assembled the mold lithium cell ten each at a time.

[Procedure amendment 7]

[Document to be Amended] Description

[Item(s) to be Amended] 0033

[Method of Amendment] Modification

[Proposed Amendment]

[0033] Here, phosphazene No.1 which is the phosphazene derivative used as an electrolytic-solution solvent is obtained by permuting the chlorine with cyclic structure (NPCl₂) of n (however, n 3-5) by three -OCH₂CH₂CH(s). phosphazene No. -- 2 and 3 are obtained by permuting the chlorine with the same cyclic structure as No.1 (NPCl₂) of n (however, n 3-5) by -OCH₂CF₂CF₃ and -OCH₂CF₂CF₂CF₂H set.

[Procedure amendment 8]

[Document to be Amended] Description

[Item(s) to be Amended] 0034

[Method of Amendment] Modification

[Proposed Amendment]

[0034] About four kinds of cells produced as mentioned above, the early cell property (an electrical potential difference, internal resistance) was evaluated, and the charge-and-discharge cycle engine performance, high-rate-discharge nature

(current dependency of discharge capacity), and safety were evaluated by the following appraisal method. A result is shown in a table 1.

[Procedure amendment 9]

[Document to be Amended] Description

[Item(s) to be Amended] 0036

[Method of Amendment] Modification

[Proposed Amendment]

[0036] High-rate-discharge nature

After performing the charge and discharge of 5 cycles and charging to 3.0V, it discharged by 50mA first, and it charged again and discharged by 500mA succeedingly. It performed this actuation at a time about two cells, the discharge capacity in each current value was calculated, and it asked for capacity retention by (500mA from discharge capacity)/at the time of discharge (it is the discharge capacity at the time of discharge at 50mA).

[Procedure amendment 10]

[Document to be Amended] Description

[Item(s) to be Amended] 0038

[Method of Amendment] Modification

[Proposed Amendment]

[0038]

[A table 1]

		電 解 液 溶 媒		電池初期特性		サイクル性能			高 率 放 電 性			安 全 性
		溶 媒 種	粘 度 (cP)	電 圧 (V)	内 部 抵 抗 (mΩ)	初 期 (mAh)	50 サイクル (mAh)	保持率 (%)	50mA (mAh)	500mA (mAh)	保持率 (%)	
実 施 例	1	ホスファゼン No.1	60	3.32	210	745	708	95	745	660	89	全 く な し
	2	ホスファゼン No.2	100	3.28	220	750	705	94	750	660	88	全 く な し
比 較 例	1	ホスファゼン No.3	400	3.26	400	690	585	85	690	470	68	全 く な し
	2	プロピレンカーボネート + エチレンカーボネート*	20	3.33	180	760	730	96	760	690	91	3本も液も2本破裂

*両溶媒を50体積%ずつ混合

[Procedure amendment 11]

[Document to be Amended] Description

[Item(s) to be Amended] 0039

[Method of Amendment] Modification

[Proposed Amendment]

[0039] As shown in a table 1, the conventional cell (example 2 of a comparison) using the organic solvent as an electrolytic-solution solvent The cell (examples 1 and 2) using the phosphazene derivative of moderate viscosity as an electrolytic-solution solvent to having caused a liquid spill, a burst, and ignition at the time of a short circuit There are no abnormalities also at the time of a short circuit, and it turns out at it that it is not inferior even if it compares with the conventional cell using an organic solvent about a dramatically safe thing and the cell engine performance.

[Procedure amendment 12]

[Document to be Amended] Description

[Item(s) to be Amended] 0040

[Method of Amendment] Deletion

[Procedure amendment 13]

[Document to be Amended] Description

[Item(s) to be Amended] 0041

[Method of Amendment] Modification

[Proposed Amendment]

[0041] Moreover, although abnormalities, such as ignition, were not seen like examples 1 and 2 at the time of a short circuit by the cell (example 1 of a comparison) using the phosphazene derivative with which viscosity exceeds 300cP(s) as an electrolytic-solution solvent, since solvent viscosity is too high, the discharge capacity under a high current is in the inclination to decrease considerably and for the cycle engine performance to be also inferior.

[Procedure amendment 14]

[Document to be Amended] Description

[Item(s) to be Amended] 0042

[Method of Amendment] Modification

[Proposed Amendment]

[0042] The cell which has the same structure as examples 1 and 2 was assembled using the electrolyte which dissolved LiPF₆ in the same positive-electrode ingredient and same negative-electrode ingredient as examples 3-5 and the [example 3 of comparison] examples 1 and 2, and four kinds of each electrolytic-solution solvent shown in a table 2 by the concentration of 0.5 mols/kg every ten per one kind of above-mentioned electrolytic-solution solvent.

[Procedure amendment 15]

[Document to be Amended] Description

[Item(s) to be Amended] 0043

[Method of Amendment] Modification

[Proposed Amendment]

[0043] Here, what was obtained by permuting the chlorine with cyclic structure (NPCl₂) of n (however, n 3-5) by three -OCH₂CH₂CH(s) as a phosphazene derivative was used.

[Procedure amendment 16]

[Document to be Amended] Description

[Item(s) to be Amended] 0045

[Method of Amendment] Modification

[Proposed Amendment]

[0045] The same assessment as an example 1 was performed about four kinds of cells produced as mentioned above. A result is written together to a table 2.

[Procedure amendment 17]

[Document to be Amended] Description

[Item(s) to be Amended] 0046

[Method of Amendment] Modification

[Proposed Amendment]

[0046]

[A table 2]

		電 解 液 溶 媒		電池初期特性		サイクル性能			高 率 放 電 性			安 全 性
		溶 媒 種 (体積%/体積%)	粘 度 (cP)	電 圧 (V)	内 部 抵 抗 (mΩ)	初 期 (mAh)	50サイ クル (mAh)	保持率 (%)	50mA (mAh)	500mA (mAh)	保持率 (%)	
実 施 例	3	環状構造ホスファゼン誘導体/ 1,2-ジメトキシエタン (60/40)	18	3.28	150	765	730	95	765	705	92	全く なし
	4	環状構造ホスファゼン誘導体/ 1,2-ジメトキシエタン (75/25)	24	3.32	170	760	720	95	760	685	90	全く なし
	5	環状構造ホスファゼン誘導体/ 1,2-ジメトキシエタン (85/15)	32	3.24	185	760	705	93	760	675	89	全く なし
比 較 例	3	プロピレンカーボネート/1,2-ジメトキシエタン (50/50)	10	3.30	140	770	740	96	770	725	94	2本も 3本も 破裂

[Procedure amendment 18]

[Document to be Amended] Description

[Item(s) to be Amended] 0047

[Method of Amendment] Modification

[Proposed Amendment]

[0047] As shown in a table 2, the cell (example 3 of a comparison) using the electrolytic-solution solvent which consists only of an aprotic organic solvent The cell (examples 3-5) using the mixture of a phosphazene derivative and an aprotic organic solvent as an electrolytic-solution solvent to having caused a liquid spill, a burst, and ignition at the time of a short circuit There are no abnormalities also at the time of a short circuit, and it turns out at it that it is not inferior even if it compares with the conventional cell using an organic solvent about a dramatically safe thing and the cell engine performance.

[Procedure amendment 19]

[Document to be Amended] Description

[Item(s) to be Amended] 0048

[Method of Amendment] Deletion

[Translation done.]